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Citation style: Starowicz P., Kurleto R., Goraus Jerzy, Walczak L., Penc B., Adell J., Szlawska M., Kaczorowski D., Szytula A. (2014). Valence band of Ce2Co0.8Si3.2 and Ce2RhSi3 studied by resonant photoemission spectroscopy and FPLO calculations. "Acta Physica Polonica A" (Vol. 126, nr 4A (2014), s. A144-A147), doi 10.12693/APhysPolA.126.A-144

Proceedings of the XVI National Conference on Superconductivity and Strongly Correlated Systems, Zakopane 2013

Valence Band of $Ce_2Co_{0.8}Si_{3.2}$ and Ce_2RhSi_3 Studied by Resonant Photoemission Spectroscopy and FPLO Calculations

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This work presents studies of the valence band of two Kondo lattice systems: $Ce_2Co_{0.8}Si_{3.2}$, which is paramagnetic with the Kondo temperature $T_K \approx 50$ K and Ce_2RhSi_3, which is antiferromagnetic below $T_N = 4.5$ K and exhibits $T_K \approx 9$ K. The photoemission spectra, which are obtained with photon energy tuned to Ce $4d$–$4f$ resonance, reveal a Kondo peak at the Fermi energy (E_F), its spin–orbit splitting partner at 0.24 eV and a broad maximum related to Ce f^0 final state. The spectra indicate that Kondo peak has a higher intensity for $Ce_2Co_{0.8}Si_{3.2}$. The off-resonance photoemission data reveal that a maximum in the $3d$ electron density of states is shifted towards E_F for $Ce_2Co_{0.8}Si_{3.2}$ as compared to Ce_2RhSi_3. Full-potential local-orbital calculations were realized with local spin density approach $+U$ approach for 213 stoichiometry. They show that a higher density of states near E_F is observed for Ce_2CoSi_3. The calculations also reveal the existing tendencies for antiferromagnetic and ferromagnetic ground states in a case of Ce_2RhSi_3 and Ce_2CoSi_3, respectively.

DOI: 10.12693/APhysPolA.126.A-144
PACS: 71.27.+a, 75.30.Mb, 71.20.Eh, 74.25.Jb

1. Introduction

Cerium intermetallics exhibit a variety of ground states depending on the role played by Ce $4f$ electrons [1]. These electrons may possess magnetic moments in magnetically ordered phases, participate in the formation of a Kondo singlet, form heavy fermion ground states, or even are incorporated in wider bands. The first important factor determining these phenomena is hybridization between f-electrons and conduction band electrons, based on the Kondo effect. The second important factor is the Ruderman–Kittel–Kasuya–Yosida (RKKY) exchange interaction. Strength of these interactions can be modified by chemical doping, pressure, magnetic field, etc., which can lead to quantum phase transitions (QPTs) between different ground states, with all the fundamental and exciting problems behind [2].

The investigated compounds, Ce_2RhSi_3 and $Ce_2Co_{0.8}Si_{3.2}$, crystallize in a hexagonal structure derived from AlB_2 type (Fig. 1). The space group is $P6/mmm$ and the lattice parameters are $a = 8.2240(12)$ Å and $c = 4.2261(8)$ Å [3]. Cerium atoms occupy two Wyckoff positions 1a (Ce1) and 3f (Ce2). $Ce_2Co_{0.8}Si_{3.2}$ with the lattice constants $a = 8.1037(7)$ Å and $c = 4.2204(3)$ Å was reported to be isostructural to Ce_2RhSi_3 [4]. In this compound, the Wyckoff 2d position is occupied by 80% of Co and 20% of Si, although the target stoichiometry in single crystal growth was Ce_2CoSi_3 [4].

Ce_2RhSi_3 is a Kondo lattice system with antiferromagnetic order below $T_N = 4.5$ K [3], low Kondo temperature

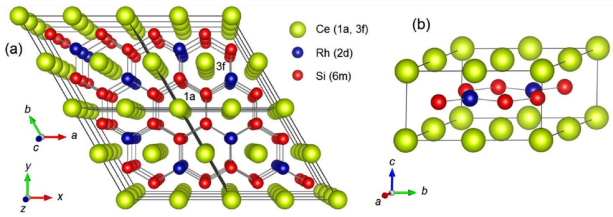

Fig. 1. Crystal structure of Ce_2RhSi_3: (a) overview along c crystallographic axis, (b) a single unit cell. Atoms and their Wyckoff positions are shown. Two different coordinations of Ce atoms correspond to 1a and 3f Wyckoff positions.

$T_K \approx 9$ K and enhanced electronic specific heat $C/T = 290$ mJ/(mol$_{Ce}$ K^2) at 0.4 K. In turn, $Ce_2Co_{0.8}Si_{3.2}$ is paramagnetic down to 0.4 K. It exhibits properties of a Kondo lattice with coherence temperature of about 80 K, the Kondo temperature $T_K \approx 50$ K and large electronic specific heat $C/T = 200$ mJ/(mol$_{Ce}$ K^2) at 0.4 K [4]. Different ground states in Ce_2RhSi_3 and Ce_2CoSi_3 motivated searching for QPT in the solid solution $Ce_2Rh_{1-x}Co_xSi_3$ [5]. However, as demonstrated in the recent study on a single crystal of $Ce_2Co_{0.4}Rh_{0.4}Si_3$ [6], inherent atomic disorder prevents the occurrence of QPT and leads at low temperatures to the formation of a Griffiths phase.

Photoemission spectroscopy (PES) can deliver a single particle spectral function, which provides a more direct insight into the Kondo effect. Previous PES studies

indicated the presence of a Kondo resonance in antiferromagnetic Ce_2RhSi_3 [7] and paramagnetic Ce_2CoSi_3 [8]. It appears that the Kondo resonance has higher intensity for Ce_2CoSi_3 when compared to Ce_2RhSi_3 system with coexisting magnetic order and Kondo interaction [9]. Recently, a momentum dependence of the Kondo peak was established in $Ce_2Co_{0.8}Si_{3.2}$ by means of angle-resolved photoemission spectroscopy (ARPES) [10]. This finding was interpreted as the evidence of a strong momentum dependence of the hybridization between conduction band and $4f$ electrons.

In the current paper our investigations are focused on the electronic valence band structure of antiferromagnetic (Ce_2RhSi_3) and paramagnetic ($Ce_2Co_{0.8}Si_{3.2}$) Kondo lattices. Resonant Ce $4d \rightarrow 4f$ photoemission spectroscopy delivers a contribution of the Ce $4f$ states to the valence band. The results are compared to theoretical calculations performed by means of full-potential local-orbital (FPLO) code.

2. Experimental

Single crystals of Ce_2RhSi_3 and $Ce_2Co_{0.8}Si_{3.2}$ were grown by the Czochralski pulling method in a tetra--arc furnace. Their synthesis and detailed characterization was described elsewhere [3, 4]. Studies of resonant photoemission spectroscopy (RESPES) were conducted at MAX-lab, Lund University, using I4 beamline of the MAX III storage ring [11]. The crystals were measured at 100 K with incident photon energies between 80 eV and 140 eV. Photoelectrons were recorded by SPECS Phoibos 100 electron analyzer with the total energy resolution of 80 meV. Band structure calculations were performed by the scalar relativistic version of the FPLO code [12] with the Perdew–Wang exchange-correlation potential [13]. Local spin-density approximation (LSDA) $+U$ was used with the around-mean-field scheme [14].

3. Results and discussion

Ce_2RhSi_3 and $Ce_2Co_{0.8}Si_{3.2}$ were investigated by means of RESPES at the Ce $4d \rightarrow 4f$ absorption edge, which occurs at the incident photon energy of approximately 120 eV. The spectra recorded with the photon energy $h\nu = 120$ eV (Fig. 2) are characterized with the enhanced intensity from Ce $4f$ electrons when compared to the data obtained with the off-resonance photon energy, e.g. $h\nu = 114$ eV. The data were partially angle integrated. One can distinguish the Kondo peak observed near the Fermi energy ($f^1_{5/2}$ final state), the peak related to $f^1_{7/2}$ final state at 0.24 eV and a broad peak with contribution from f^0. The Kondo peak intensity is clearly higher for $Ce_2Co_{0.8}Si_{3.2}$, in line with stronger hybridization in this compound. This agrees with the previous PES studies [9]. The off-resonance spectra are dominated by 3d electrons from Co and Rh. It is observed in the off-resonance spectra that for $Ce_2Co_{0.8}Si_{3.2}$ the maximum in density of states (DOS) is closer to E_F than in the case of Ce_2RhSi_3. The present results of resonant photoemission are in qualitative agreement with the recent ARPES studies carried out for $Ce_2Co_{0.8}Si_{3.2}$ [10]. Previously, the $f^1_{5/2}$ and $f^1_{7/2}$ peaks were found to be nondispersive. A broad peak around binding energy of 2 eV was attributed to electrons from the Ce f^0 final states and the Co $3d$ states [10].

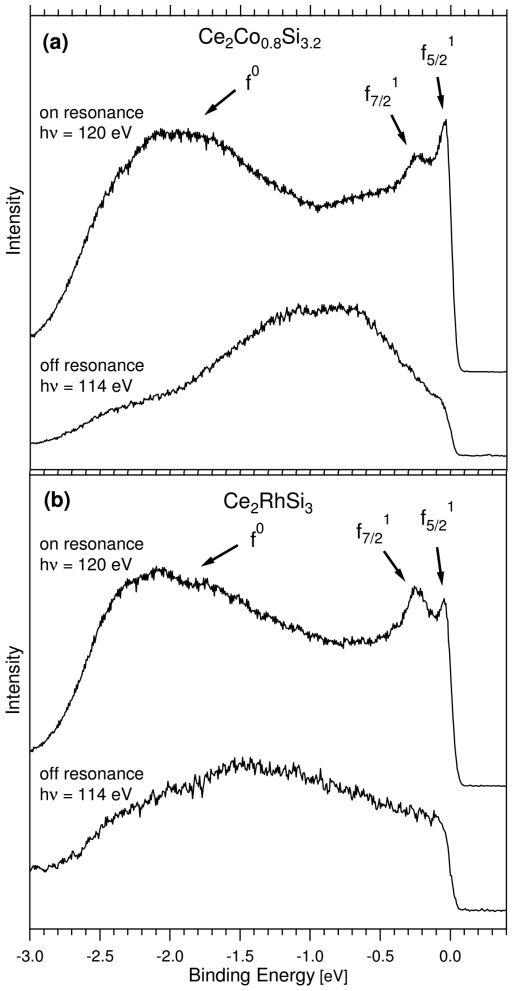

Fig. 2. Resonant photoemission spectra obtained for (a) $Ce_2Co_{0.8}Si_{3.2}$ and (b) Ce_2RhSi_3 with photon energies: $h\nu = 120$ eV (on Ce $4d \rightarrow 4f$ resonance) and $h\nu = 114$ eV (off Ce $4d \rightarrow 4f$ resonance) at the temperature $T = 100$ K.

Theoretical calculations were performed for both Ce_2RhSi_3 and Ce_2CoSi_3 (here assuming ideal 213 stoichiometry) by means of FPLO with LSDA+U approximation. They were realized with $U_{4f} = 0$ and $U_{4f} = 6$ eV and for the ground states with parallel (ferromagnetic) and antiparallel (antiferromagnetic) orientation of the Ce magnetic moments. For Ce_2RhSi_3, the ground state energy was found lower for antiferromagnetic arrangement, whereas ferromagnetic orientation was found favored for Ce_2CoSi_3.

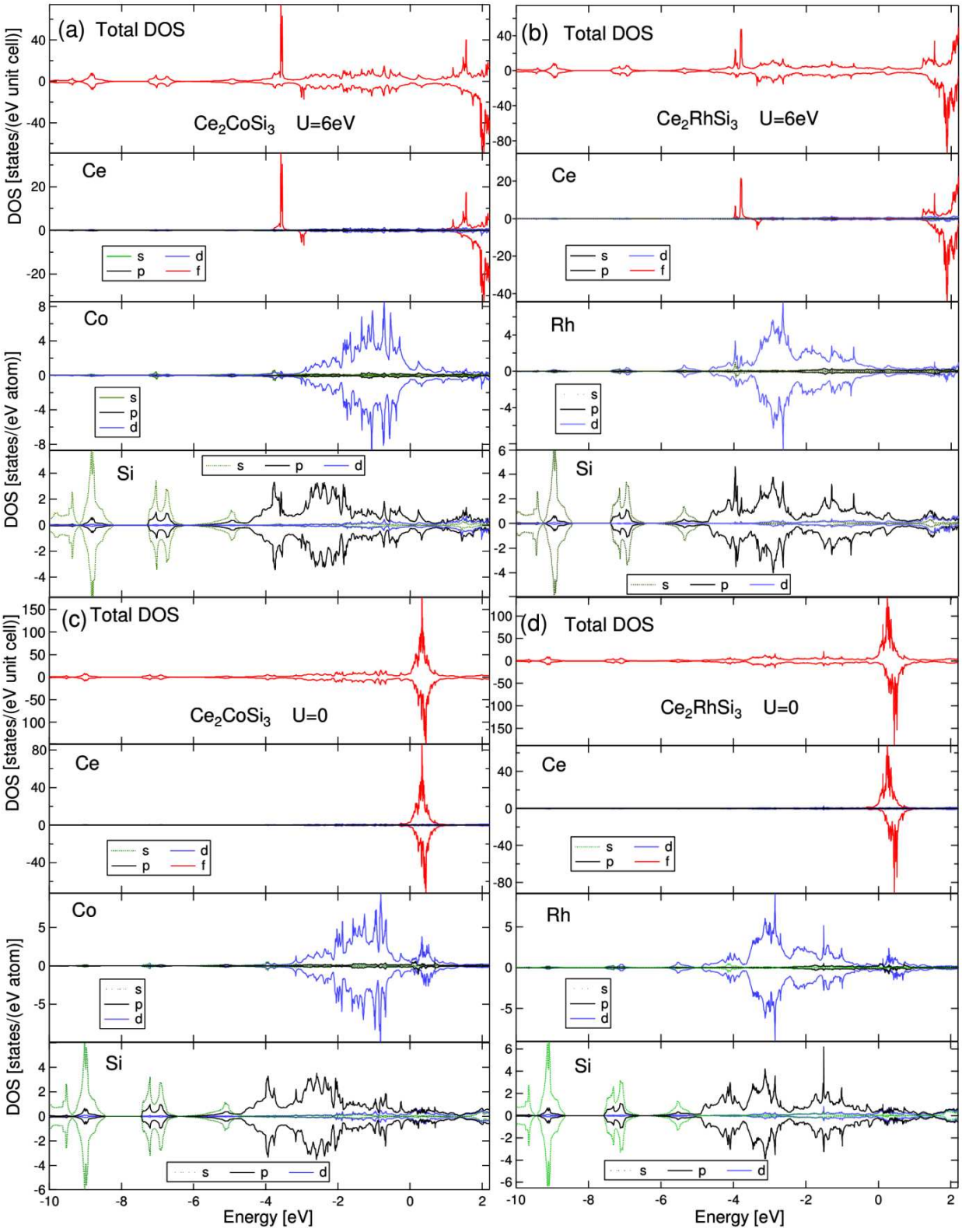

Fig. 3. Total and partial (corresponding to particular orbitals) densities of states (DOS) calculated by means of FPLO method for Ce_2CoSi_3 and Ce_2RhSi_3. LSDA+U approximation was applied with the parameter $U = 0$ and $U = 6$ eV.

The gain in energy due to the preferred magnetic order yielded for Ce_2RhSi_3 the theoretical Néel temperature $T_{N-theor} = 11.8$ K. The theoretical value of the Curie temperature in Ce_2CoSi_3 was $T_{C-theor} = 12.3$ K. $T_{N-theor}$ is quite higher than the real T_N value. On the other hand, ferromagnetic order is not realized in $Ce_2Co_{0.8}Si_{3.2}$. These results indicate certain tendencies for magnetic ordering existing in the considered materials. However, in the real systems the Kondo interaction competing with RKKY magnetic exchange results in partial or full suppression of the magnetic order. The saturation magnetic moment on Ce obtained from the calculations with $U_{4f} = 6$ eV amounted to 1.0 μ_B for both compounds. It is in reasonable agreement with the experimental value from neutron diffraction, which equals 1.3 μ_B per Ce atom [15]. Magnetic moments received from the calculations with $U_{4f} = 0$ are between 0.02 and 0.36 μ_B per Ce depending on the crystallographic site and the compound.

Figure 3 displays the total density of states (DOS) and partial DOS associated with particular orbitals obtained from FPLO calculations with LSDA+U. The results for Ce_2CoSi_3 with $U_{4f} = 0$ and $U_{4f} = 6$ eV are shown for the antiferromagnetic ground state. The same is for Ce_2RhSi_3 with $U_{4f} = 6$ eV. However, in the case of Ce_2RhSi_3 and $U_{4f} = 0$ the calculations always converged to the ferromagnetic ground state. In fact, for $U_{4f} = 0$, difference in the total energy between the parallel and antiparallel orientation of the Ce magnetic moments is very small and a choice of magnetic ordering may be random.

Partial DOS (Fig. 3) related to the Ce $4f$ orbitals is dominated by a peak at 0.3–0.4 eV above the Fermi energy for $U_{4f} = 0$. The increase of U_{4f} to 6 eV splits and redistributes the $4f$ spectral weight. The calculated results indicate that the Co $3d$ and Rh $3d$ states have an important contribution to the valence band near E_F. In turn, the Si $3p$ states are located at relatively high binding energy. It is noteworthy that the $3d$ electrons of Co are closer to E_F and yield higher DOS near E_F as compared to the Rh $3d$ states. This finding is in agreement with our resonant PES results (Fig. 2).

4. Conclusions

$Ce_2Co_{0.8}Si_{3.2}$ and Ce_2RhSi_3 were studied by means of resonant photoemission spectroscopy at the Ce $4d \rightarrow 4f$ absorption edge. The on-resonance spectra revealed enhanced contribution from the Ce $4f$ states. $Ce_2Co_{0.8}Si_{3.2}$ exhibits a more distinct Kondo peak in the on-resonance studies. For the Co-bearing system, a maximum of valence band intensity is shifted towards E_F, which is seen in both off-resonance measurements and FPLO calculations. These results imply that $Ce_2Co_{0.8}Si_{3.2}$ has higher DOS in a vicinity of the Fermi level and exhibits stronger f-ligand hybridization. The transition from antiferromagnetic Kondo lattice Ce_2RhSi_3 to paramagnetic Kondo lattice $Ce_2Co_{0.8}Si_{3.2}$ is thus accompanied by the increase in carrier density in the valence band near E_F.

Acknowledgments

We would like to thank T. Balasubramanian for help in performing the experiment. This work has been supported by the Ministry of Science and Higher Education in Poland within the grant no. N N202 201 039. J.G. acknowledges the financial support from the National Science Centre (NCN), on the basis of decision No. DEC-2012/07/B/ST3/03027.

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